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Effect of Structure and Conformation on Raman Trace Scattering Intensities in Hydrocarbons

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The ab initio (HF/D95**) optimized geometries and equilibrium molecular polarizabilities have been obtained for 35 hydrocarbons: all-*trans* straight-chain alkanes to C_{15}, isobutane, 6 cyclo- and methylcycloalkanes, 8 bicycloalkanes, 4 propellanes, and a tetracyclane. The derivative of the molecular polarizability associated with the stretch of a single CH bond has been calculated for each unique CH. In contrast to expectations of the bond polarizability model, there is considerable variation in the magnitude of the derivatives, ranging from a high of 1.38×10^{-30} C m/V for the bridgehead CH bond in bicyclo[1.1.1]pentane to a low of 0.908 $\times 10^{-30}$ C m/V for a methylene CH in bicyclo[3.3.1]nonane. These differences would result in a factor of ~2.3 difference in the Raman scattering intensity for the respective CH stretching vibrations. Trends in the equilibrium polarizabilities and in the derivatives are analyzed in terms of molecular structure and charge flow. Principal factors governing the magnitude of the derivative are identified as location, alignment, group strain, and steric hindrance. Averaging of competing effects is also inferred. Implications for the prediction and interpretation of Raman scattering intensities and for the analysis of charge flow in hydrocarbons are discussed.

Introduction

Absolute Raman trace scattering intensities are difficult to measure, and there are few experimental data. Given the proliferation of software that permits the prediction of both frequencies and intensities, simple interpretive models are of considerable importance. For several years, we have studied the Raman trace scattering spectra of small hydrocarbons, both through experiment and through ab initio molecular orbital (MO) calculations, to gain greater insight into the relationship between molecular structure and scattering intensity. The results provide a useful indication of the level of theory required to model experiment for a higher order electrical property. In the longer term, they will enable us to examine intensities in much more complex systems, such as lipid bilayers, waxes, and polymers with nonlinear optical properties.

Within the assumptions of the Placzek polarizability theory,[1] the Raman differential scattering cross section depends on the magnitude of the change in the molecular polarizability tensor during a vibration:

$$\frac{\partial\sigma}{\partial\Omega} \propto \underset{\text{isotropic}}{45\left(\frac{\partial\bar{\alpha}}{\partial q}\right)^2} + \underset{\text{anisotropic}}{7\left(\frac{\partial\gamma}{\partial q}\right)^2} \tag{1}$$

The trace, or isotropic, Raman scattering is due to the change in the mean molecular polarizability, $\partial\bar{\alpha}/\partial q$, where

$$\frac{\partial\bar{\alpha}}{\partial q} = \frac{1}{3}\left(\frac{\partial\alpha_{xx}}{\partial q} + \frac{\partial\alpha_{yy}}{\partial q} + \frac{\partial\alpha_{zz}}{\partial q}\right) \tag{2}$$

and is nonzero only for totally symmetric modes. We have restricted our studies to the trace scattering since it affords narrow, well-resolved bands, and the intensity parameters are isotopically invariant. Experimental measurement of the absolute scattering intensities of the saturated hydrocarbons, methane, ethane, and propane;[2] butane (*trans* and *gauche* conformers);[3] pentane (*trans*−*trans*, *gauche*−*trans*, and *gauche*−*gauche* conformers);[4] and cyclohexane,[5] revealed previously unsuspected variations in $\partial\bar{\alpha}/\partial r_{CH}$, the derivative of the mean molecular polarizability associated with the stretch of a single CH bond. We have concluded that the absolute Raman trace scattering intensity for a CH stretching vibration is correlated with the position and orientation of the CH bond within the molecule, as well as with conformation. The experimental results are mirrored by the MO calculations of the derivative at the Hartree−Fock level. To get a better understanding of the structural origin of these differences, the MO wave functions have been analyzed with the theory of atoms in molecules (AIM).[2,4−6] This approach has successfully provided a model to describe polarizability derivatives in terms of intramolecular charge flow, both as transfer between atoms and as reorientation within an atomic basin.

Following the analysis of the small hydrocarbons, we wished to address several questions. First, do the variations in $\partial\bar{\alpha}/\partial r_{CH}$ that we have discovered so far represent the extremes, or will even greater changes become apparent as the size and complexity of the molecules increase? Second, is there a reasonable explanation for the variations, one which can be based on molecular structure? The molecules to be examined should exhibit varied stereochemistry that will clarify the relationship between $\partial\bar{\alpha}/\partial r_{CH}$ and structure. To that end, we have now extended the ab initio study to a set of 35 hydrocarbons comprised of the all-*trans* *n*-alkanes up to C_{15}, isobutane, 6 cyclo- and methylcycloalkanes, 8 bicycloalkanes, four propellanes, and a tetracyclane. The calculated values of $\partial\bar{\alpha}/\partial r_{CH}$ have been obtained for each symmetrically unique CH bond.

An earlier model for the empirical treatment of Raman scattering intensities, the bond polarizability model,[7−9] assumes

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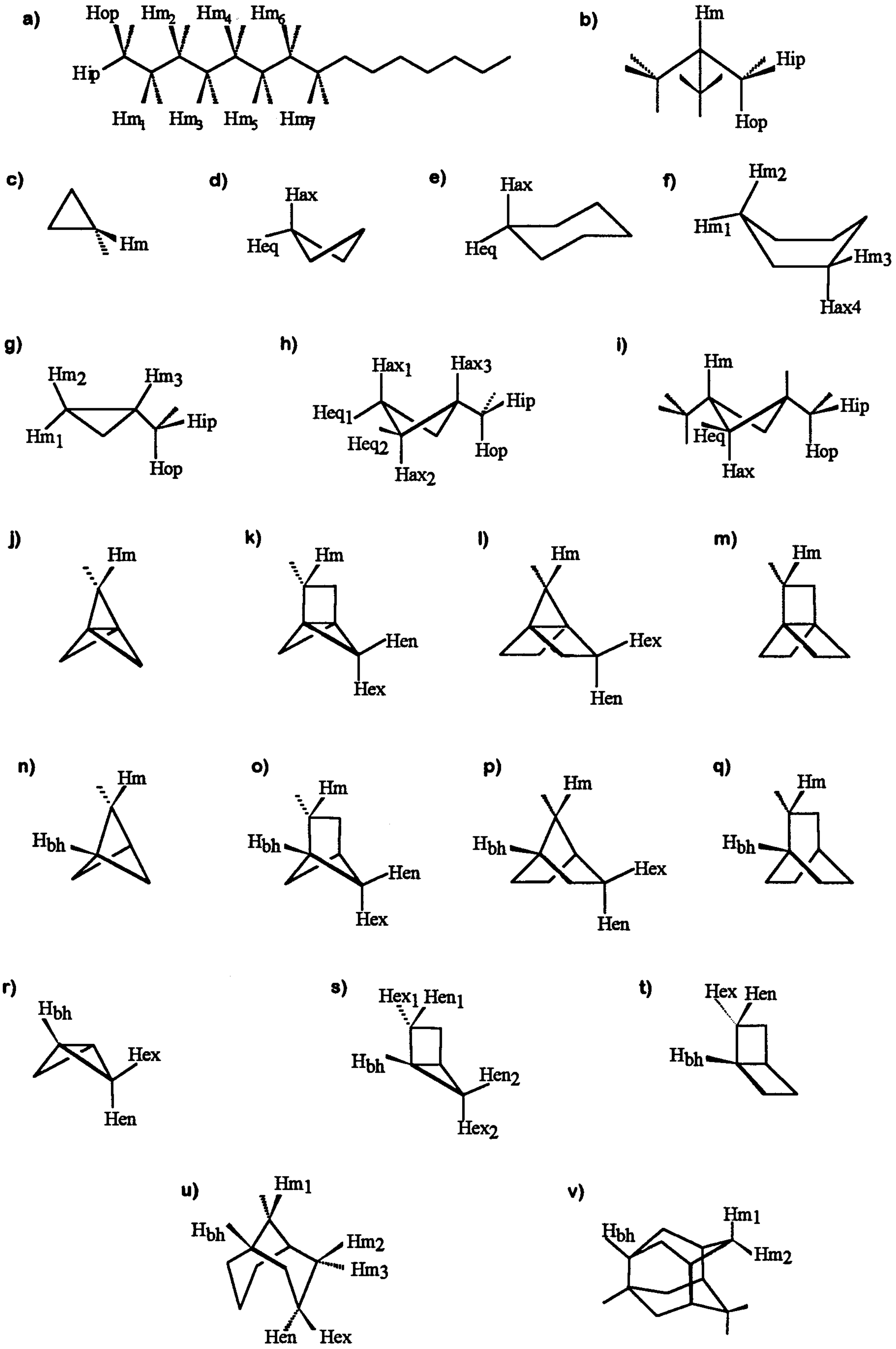


Figure 1. Molecular structures showing unique CH bonds and labels.

that the total molecular polarizability may be adequately represented as the sum of bond polarizability ellipsoids, each oriented along a bond. In the first approximation, these ellipsoids have cylindrical symmetry about the bond and are noninteracting. Raman scattering intensities, due to $\partial\bar{\alpha}$(molecule), are ascribed to $\partial\bar{\alpha}$(bond). The latter parameters are obtained in an empirical fit to the observed intensities and have been assumed to be transferable between molecules. It was hoped that the present study would illustrate why this assumption has sometimes been found to work, while simultaneously highlighting the cases where it must fail.

In addition to addressing these issues, we hope to be able to identify very simple molecules in which a large variation in $\partial\bar{\alpha}/\partial r_{CH}$ is predicted to occur. Such molecules would be likely candidates for experimental investigation to test the predictions. The derivative is a measure of how easily charge will flow in a molecule. If we can now predict these subtle differences, then, coupled with the AIM analysis, the derivative becomes a sensitive probe of where charge will flow within a molecule, and why.

Calculation Method

The calculation method is the same as that used previously[2,4,5] and is outlined briefly here. All MO calculations are performed with Gaussian 94,[10] at the Hartree−Fock level of theory, since we have found that electron correlation is not important for saturated hydrocarbons.[11] As in previous calculations, we have used the D95** basis set.[12,13] While the resultant polarizabilities and derivatives slightly underestimate the experimental values, they have been found to faithfully reproduce the relative values and trends.[2−5,11,20]

Several MO programs, including the Gaussian series, have the capability to produce infrared and Raman intensities in terms of the normal coordinates, $\partial\bar{\alpha}/\partial q$. However, we are interested in getting the derivatives in terms of internal coordinates, $\partial\bar{\alpha}/\partial r_{CH}$. The former may be converted to internal coordinates through standard harmonic force-field methods, but these procedures are cumbersome for some of the molecules under consideration. It is easier to obtain the $\partial\bar{\alpha}/\partial r_{CH}$ directly by finite difference, as described in steps 1−5. In our previous work,[2,4,5] we have found no quantitative difference between the analytic and finite difference methods.

1. Use Gaussian 94, with D95** basis set, to get the optimized geometry
2. Calculate the equilibrium polarizability tensor at that geometry: α
3. Stretch all symmetrically equivalent CH bonds by +0.010 Å; i.e., displace hydrogen nuclei along a symmetry coordinate
4. Recalculate the molecular polarizability at the new geometry: α'
5. Evaluate the derivative by finite difference

$$\frac{\partial\bar{\alpha}}{\partial r_{CH}} \cong \frac{\Delta\alpha}{\Delta r_{CH}} = \frac{1}{n}\left(\frac{\bar{\alpha}' - \bar{\alpha}}{\Delta r_{CH}}\right) \tag{3}$$

where n = number of symmetrically equivalent CH bonds stretched in step 3.

Molecular Structures

The molecules in this study have been selected for their range of stereochemical features. The structures and designations for the unique CH bonds are shown in Figure 1. The *n*-alkanes in the all-*trans* conformation are represented by pentadecane, **a**. The methyl groups possess two types of CH bond: one lying in the plane of the carbon skeleton, designated Hip, and two lying above and below, designated Hop (out-of-plane). These labels are applied to all methyl groups, as appropriate. The methylene CH are labeled Hm_n, where $n = 1$ indicates the methylene adjacent to the methyl group. Isobutane (**b**) is the only branched acyclic alkane. For the ring (**c**−**i**), propellane (**j**−**m**), bi- (**n**−**u**), and tetracycloalkane (**v**) structures, the designations are descriptive wherever obvious (Hax, Heq for axial, equatorial; Hex, Hen for exo, endo; Hbh for bridgehead). In all other cases, both methylene and methine are denoted as Hm; where more than one type occurs, they are numbered for convenience.

Results and Discussion

We begin with an examination of the equilibrium molecular polarizabilities and, through the AIM analysis, the structural dependence of charge flow. Polarizability derivatives are then interpreted in relation to previous AIM analyses. In order to make some sense of the variations, it is necessary to identify the competing factors that determine the magnitude of the derivative in each case. We seek these through an examination of the different homologous series: straight chains, cycloalkanes, methylcycloalkanes, propellanes, and bi- and tetracyclic alkanes. In the discussion of the variations, we take the value of $\partial\bar{\alpha}/\partial r_{CH}$ for methane, 1.045×10^{-30} C m/V, as a benchmark. After considering the different series, we will summarize common stereochemical features associated with enhancement or reduction of the derivative. Finally, we compare the present results with the assumptions of the bond polarizability model.

Molecular Polarizabilities. The first two steps in our procedure yield D95** values for $\bar{\alpha}$ of the 35 molecules. These are listed in Table 1, along with the optimized energies and, where available, the molecular volumes determined using the theory of atoms in molecules.[6] Molecular polarizability is a measure of the magnitude of the dipole moment (μ) induced in a molecule when an electric field (E) is applied:

$$\mu = \alpha E \tag{4}$$

Equation 4, when α is expressed in Å^3, is isomorphic to that defining the dipole moment induced in a perfectly conducting sphere by an external field:[14]

$$\mu = r^3 E \tag{5}$$

In our previous work, we found a linear relationship between α and volume for several small molecules, ranging in size from H_2 to cyclohexane.[2,4−6,15] For some simple alkanes, it has been established that the energy and volume of similar atoms or groups are transferable and scale linearly.[6] For example, the energy and molecular volume of cyclohexane[5] are very well approximated by six times the corresponding properties of the first CH_2 in *n*-pentane:[15−17] E = 39.0120 au (*n*-pentane), 39.0379 au (cyclohexane); volume = 157.82 au (*n*-pentane), 158.19 au (cyclohexane). We would like to plot $\bar{\alpha}$ versus volume for the molecules in this study, but the AIM volumes are available only for the straight-chain alkanes.[18,19] Instead, we have plotted polarizability as a function of total molecular energy for all molecules (Figure 2). For the straight-chain alkanes, the correlation coefficient between $\bar{\alpha}$ and E is 0.994, confirming the group transferability. The linear regression fits for the cyclic, bridged, and propellane systems have slightly different slopes and intercepts. The increased strain in these systems, especially at the bridgehead carbons, creates an unusual electronic charge distribution.[18,19] The expanded portion of the plot (see inset, Figure 2) shows that for similar numbers of carbon atoms, the polarizability decreases with increasing strain

TABLE 1: Equilibrium Molecular Polarizabilities and Energies at Optimized Geometries (HF/D95)**

molecule[a]	energy[b]	α[c]	molecule	energy[b]	α[c]
methane	−40.208	12.115	cyclohexane (chair) (**e**)	−234.258	58.915
ethane	−79.249	22.441	cyclohexane (boat) (**f**)	−234.246	58.600
propane	−118.292	32.629	methylcyclopropane (**g**)	−156.130	40.501
butane	−157.336	42.844	methylcyclobutane (**h**)	−195.177	50.461
pentane	−196.379	53.099	dimethylcyclobutane (**i**)	−234.223	60.796
hexane	−235.422	63.441	[1.1.1]propellane (**j**)	−192.729	46.265
heptane	−274.465	73.851	[2.1.1]propellane (**k**)	−231.768	56.136
octane	−313.508	84.307	[2.2.1]propellane (**l**)	−270.814	64.021
nonane	−352.551	94.799	[2.2.2]propellane (**m**)	−309.871	73.532
decane	−391.594	105.323	bicyclo[1.1.1]pentane (**n**)	−193.945	47.352
undecane	−430.637	115.867	bicyclo[2.1.1]hexane (**o**)	−233.037	56.618
dodecane	−469.680	126.427	bicyclo[2.2.1]heptane (**p**)	−272.118	65.321
tridecane	−508.723	136.999	bicyclo[2.2.2]octane (**q**)	−311.168	74.454
tetradecane	−547.766	147.581	bicyclo[1.1.0]butane (**r**)	−154.902	37.700
pentadecane (**a**)	−586.809	158.173	bicyclo[2.1.0]pentane (**s**)	−193.966	47.087
isobutane (**b**)	−157.344	42.757	bicyclo[2.2.0]hexane (**t**)	−233.014	56.435
cyclopropane (**c**)	−117.085	30.391	bicyclo[3.3.1]nonane (**u**)	−350.214	84.641
cyclobutane (**d**)	−156.132	40.172	iceane (**v**)	−465.000	105.490

[a] Letters in parentheses identify structure in Figure 1. [b] Units: au. [c] Units: 10^{-40} C m^2/V.

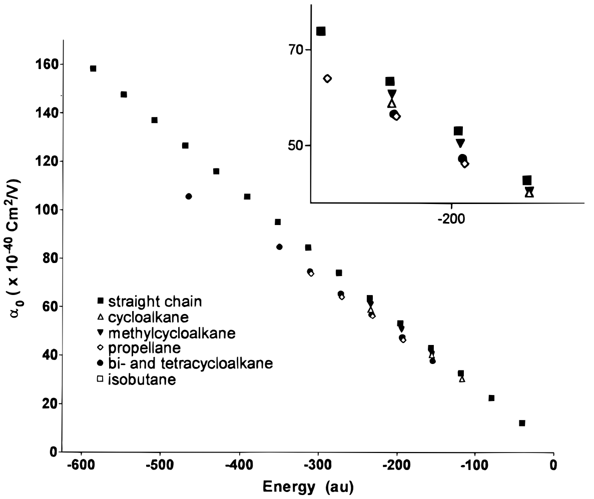


Figure 2. Variation of mean molecular polarizability of hydrocarbons with total energy from optimized HF/D95** MO calculations.

energy:

$$\alpha(\text{straight chain}) > \alpha(\text{cyclic}) > \alpha(\text{bicyclic}) \cong \alpha(\text{propellane})$$

According to the AIM theory,[6,16] the dipole induced by the applied field may be expressed as the sum of two terms:

$$\Delta\mu_{\text{induced}} = \Delta\mu_{\text{CT}} + \Delta\mu_{\text{AD}} \tag{6}$$

The first is a charge-transfer term, $\Delta\mu_{\text{CT}} = \Delta N \cdot \mathbf{r}$; the second is an atomic dipole term, $\Delta\mu_{\text{AD}}$. Both terms are calculated for each atom in the molecule and summed over all atoms to give the total induced molecular dipole. The atomic charge-transfer term is the product of ΔN, the change in the atomic electron population produced by the field, and $\mathbf{r}$, the distance of that nucleus from the molecular charge center. We found that the change in atomic electron population was significant only at the terminal atoms, decreasing at one end and increasing by an almost equal amount at the other.[2,4−6] This is analogous to the surface charge polarization of dielectric materials placed in an electric field. Charge transfer is greater along the bonds in the chain, rather than perpendicular to them, rather like $\alpha_{\parallel}$ and $\alpha_{\perp}$ in diatomic molecules. The applied field induces little change in the electron populations of the interior atoms. This is presumably because the surface charge polarization reduces the influence of the external field. Thus the $\Delta\mu_{\text{CT}}$ term for the interior atoms is very small. However, the electric charge within each atomic basin rearranges in such a way as to oppose the surface polarization. This reorientation, $\Delta\mu_{\text{AD}}$, is the second term in the total induced dipole and is quite large for interior atoms.

The individual components of the molecular polarizability (α_{xx}, α_{yy}, α_{zz}) all increase with molecular size. In the straight chains, the largest component always coincides with the axis of the carbon chain. In the cycloalkanes, the longest chain path and largest component lie in the ring plane and through any additional methyl substituents. In the bicyclics and propellanes, it follows the predominant continuous-chain direction. In conclusion, if our assumption of a direct relationship between energy and volume is correct, then the molecules studied here do seem to polarize in the manner predicted for a sphere (eqs 3 and 4). This is a little surprising, given that many, especially the long chains, are far from spherical.

Polarizability Derivatives: $\partial\bar{\alpha}/\partial r_{\text{CH}}$. The D95** derivatives of the mean molecular polarizability with respect to the stretch of each unique CH bond are listed in Table 2 for the straight-chain alkanes and Table 3 for the various (poly)cyclic alkanes. The values of $\partial\bar{\alpha}/\partial r_{\text{CH}}$ for the CH bonds in the straight chain alkanes are shown versus chain length in Figure 3. The derivatives for the CH bonds are plotted against number of carbon atoms for the remaining molecules: cycloalkanes (Figure 4), methylcycloalkanes (Figure 5), propellanes (Figure 6), bi- and tetracycloalkanes (Figure 7).

The largest calculated derivative is 1.386×10^{-30} C m/V, for the bridgehead CH bond in bicyclo[1.1.1]pentane (**n**, Table 3). Among the methylenes, the derivatives range from a high of 1.325 to a low of 0.908×10^{-30} C m/V for the Hex and Hen bonds in bicyclo[3.3.1]nonane (**u**). Since the Raman trace scattering intensity depends on the square of the polarizability derivative, eq 1, this difference would imply a factor of 2 difference in the relative intensities for these methylene CH bonds. It may appear surprising that such variation should exist when the equilibrium polarizabilities of the CH_2 groups exhibit such excellent transferability. However, the equilibrium polarizability is, in a sense, a static property—a property of the molecule at rest. The derivative is a dynamic property, providing a measure of the molecular charge redistribution when different parts of the molecule are distorted by a vibration. We now consider the homologs.

TABLE 2: Values[a] of $\partial\bar{\alpha}/\partial r_{CH}$ for Straight-Chain Alkanes Calculated at the HF/D95 Level**

molecule	Hip	Hop	Hm1	Hm2	Hm3	Hm4	Hm5	Hm6	Hm7
methane	1.045								
ethane	1.096								
propane	1.181	1.053	1.126						
butane	1.214	1.046	1.068						
pentane	1.253	1.036	1.057	1.014					
hexane	1.274	1.037	1.046	1.004					
heptane	1.292	1.035	1.046	0.991	0.992				
octane	1.303	1.036	1.043	0.991	0.981				
nonane	1.313	1.036	1.045	0.989	0.979	0.968			
decane	1.319	1.036	1.044	0.990	0.978	0.968			
undecane	1.324	1.036	1.044	0.990	0.979	0.966	0.968		
dodecane	1.328	1.036	1.044	0.991	0.979	0.967	0.967		
tridecane	1.331	1.036	1.044	0.990	0.979	0.967	0.967	0.965	
tetradecane	1.333	1.036	1.044	0.991	0.979	0.967	0.967	0.966	
pentadecane	1.335	1.036	1.044	0.991	0.979	0.967	0.967	0.965	0.966

[a] Units: 10^{-30} C m/V.

TABLE 3: Values[a] of $\partial\bar{\alpha}/\partial r_{CH}$ for Cyclic Alkanes Calculated at the HF/D95 Level**

molecule[b]	type	$\partial\bar{\alpha}/\partial r_{CH}$	molecule[b]	type	$\partial\bar{\alpha}/\partial r_{CH}$
isobutane (**b**)	Hip	1.107	[2.2.2]propellane (**m**)	Hm	1.130
	Hop	1.000	bicyclo[1.1.1]pentane (**n**)	Hbh	1.386
	Hm	1.118		Hm	1.124
cyclopropane (**c**)	Hm	1.133	bicyclo[2.1.1]hexane (**o**)	Hbh	1.298
cyclobutane (**d**)	Hax	1.111		Hen	1.145
	Heq	1.213		Hex	1.161
cyclohexane (chair) (**e**)	Hax	1.021		Hm	1.115
	Heq	1.259	bicyclo[2.2.1]heptane (**p**)	Hbh	1.264
cyclohexane (boat) (**f**)	Hm1	1.275		Hen	1.056
	Hm2	0.982		Hex	1.144
	Hm3	1.187		Hm	1.147
	Hm4	1.043	bicyclo[2.2.2]octane (**q**)	Hbh	1.285
methylcyclopropane (**g**)	Hip	1.203		Hm	1.103
	Hop	0.954	bicyclo[1.1.10]butane (**r**)	Hbh	1.216
	Hm1	1.073		Hen	1.128
	Hm2	1.184		Hex	1.156
	Hm3	1.144	bicyclo[2.1.0]pentane (**s**)	Hbh	1.250
methylcyclobutane (**h**)	Hip	1.178		Hen1	1.153
	Hop	0.967		Hen2	1.072
	Hax1	1.127		Hex1	1.180
	Hax2	1.049		Hex2	1.215
	Hax3	1.106	bicyclo[2.2.0]hexane (**t**)	Hbh	1.229
	Heq1	1.250		Hen	1.057
	Heq2	1.208		Hex	1.205
dimethylcyclobutane (**l**)	Hip	1.200	bicyclo[3.3.1]nonane (**u**)	Hbh	1.268
	Hop	0.940		Hen	0.908
	Hm	1.113		Hex	1.325
	Hax	0.995		Hm1	1.108
	Heq	1.200		Hm2	1.085
[1.1.1]propellane (**j**)	Hm	1.039		Hm3	1.162
[2.1.1]propellane (**k**)	Hm	1.107	iceane (**v**)	Hbh	1.233
	Hen	1.016		Hm1	1.130
	Hex	1.168		Hm2	1.063
[2.2.1]propellane (**l**)	Hm	1.105			
	Hen	1.081			
	Hex	1.257			

[a] Units: 10^{-30} C m/V. [b] Letter in parentheses following name corresponds to structure in Figure 1.

Straight Chain. The CH bonds in the all-*trans* conformers have already been classified as in-plane, out-of-plane, and methylene. In our previous work[2,4,15] on straight-chain alkanes up to pentane, we had observed that the values of $\partial\bar{\alpha}/\partial r_{CH}$ for the Hop and Hm positions were quite similar while the polarizability derivative for the Hip position increased with chain length. The current data indicate that this increase levels off for chain lengths beyond C_{10} (Figure 3). Our AIM analyses of propane[2,15] and pentane[4] showed that the increase for Hip was due to an increase in charge transfer between the terminal carbon atoms, when that CH bond was stretched. This change, combined with the distance over which it occurred, led to a very large charge-transfer term ($\Delta N\cdot\mathbf{r}$) in the induced dipole. This term was much smaller for both the Hop and Hm stretches. We had concluded that the greater magnitude of the polarizability derivative seemed to be associated with the alignment of the CH bond with the plane of the carbon skeleton as well as its position at the end of the chain.

A damping effect from the intervening methylenes could lead to the leveling off predicted here. Certainly, in the case of all-*trans n*-pentane, the increase in the charge-transfer term at the carbon was greatly offset by increases in the opposing μ_{AD} contributions from the interior atoms.[4] While damping would increase with number of methylenes, the charge-transfer term would also increase with the greater length, since $\mu_{CT} = \Delta N\cdot\mathbf{r}$.

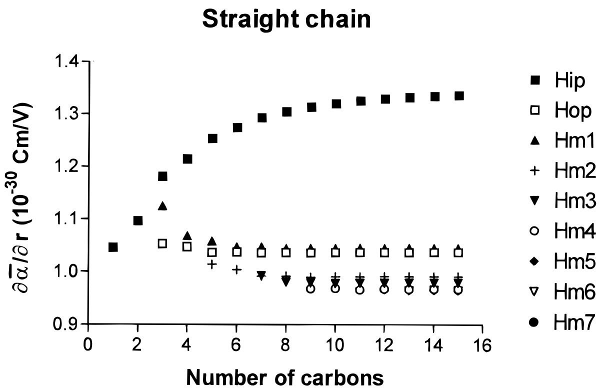


Figure 3. Calculated (HF/D95**) values of mean molecular polarizability derivative associated with the stretch of a single CH bond in straight-chain alkanes. See Figure 1 for labels.

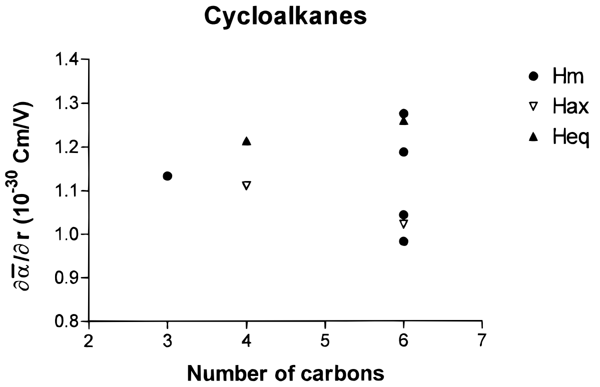


Figure 4. Calculated (HF/D95**) values of mean molecular polarizability derivative associated with the stretch of a single CH bond in cycloalkanes. See Figure 1 for labels.

According to our predicted results, the damping of the methylenes must eventually balance the charge transfer.

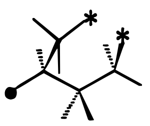
The derivatives for the Hop and Hm_1 are generally very similar and overall much lower than those for the Hip. The derivative for Hm_1 in propane is anomalously greater than that for the Hop. This puzzling difference was confirmed by experiment.[20,21] As the chain length increases, the derivative for Hm_1 gradually decreases, leveling off at a value around that of the methyl Hop. The methylene is bounded by methyl groups only in propane and is energetically unique.[6] These factors are doubtless the basis for the observed behavior. We would be interested to see how its chemical shielding tensor compares to that of other methylene groups.

In contrast to the derivative for Hip, the derivatives for Hop and Hm decrease with increasing chain length, also leveling off around C_{10}. This can be followed by comparison of the Hm_n for constant n (any column in Table 2). For a given molecule, the derivative is smallest for CH bonds in the middle of the chain. The methylene bond stretch is roughly perpendicular to the plane of the carbon skeleton, and a bond stretch exerts much the same effect on the polarizability regardless of the location of that bond along the chain.

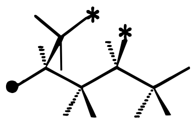
Because of their location, the three methyl groups in isobutane have two bonds that are in-plane to a carbon chain portion and only one out-of-plane, as labeled in Figure 1. The derivatives clearly exhibit the Hip and Hop characteristics. The derivative for methine CH is comparable to that of the H in ethane and the Hm in propane, as seems reasonable, given their similar molecular dimensions.

Cycloalkanes. The distinction between axial and equatorial appears in **d** and increases with ring size. The value of $\partial\bar{\alpha}/\partial r_{CH}$ is always larger for Heq (Table 3, Figure 4). The difference between the derivatives for the axial and equatorial CH was first observed experimentally in cyclohexane (**e**),[5] and the desire to understand it was one of the driving forces in initiating the present research. In the AIM analysis of the equilibrium polarizability[5] of **e**, $\Delta\mu_{CT}$ for the equatorial CH was found to be far greater than that for the axial CH. The increase in the charge-transfer term when the Heq bond is stretched is also greater than that for the Hax stretch. The Heq bond occupies an in-plane orientation to the local segment of the ring and is more nearly aligned with the ring plane. In this respect, it resembles the Hip of the straight-chain alkanes.

Since some of the polycyclic molecules possess segments corresponding to the boat form of cyclohexane, derivatives for this conformer (**f**) have also been calculated. Rotation brings two methylene groups into proximity and steric hindrance comes into play. In our analyses of the Raman trace scattering spectra of *n*-butane and *n*-pentane,[3,4,22] we found $\partial\bar{\alpha}/\partial r_{CH}$ was much smaller for the CH bonds marked with an asterisk (*) in the *gauche* conformers:



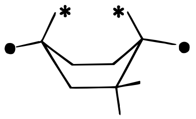
gauche **butane**



gauche-trans **pentane**

The polarizability derivative for CH* is about 0.95 × 10^{-30} C m/V, 10% lower than the benchmark value for methane. The CH* bonds are directed toward each other, and the small interatomic distance—about 2.32 Å—is indicative of steric crowding. One facet of this crowding is that the stretch of these bonds brings the atoms even closer together. However, large values of $\Delta\mu_{CT}$ have been associated mainly with bonds at the extreme ends of the molecule, moving away from each other (Hip, Heq). A second facet is the correlation between polarizability and molecular volume. The CH stretching motion tends toward the interior of the molecule and is not likely to increase the van der Waals volume greatly. With the combination of these factors, a smaller $\partial\bar{\alpha}/\partial r_{CH}$ is perhaps not unreasonable. Note that the CH bonds marked ● have been rotated to an in-plane orientation at the end of a chain fragment. As expected, the $\partial\bar{\alpha}/\partial r_{CH}$ for these bonds (1.20 × 10^{-30} C m/V) has increased relative to the benchmark value.

The boat form (**f**) brings the Hm_2 (*) into a similarly sterically crowded situation:



The interatomic distance is only 2.35 Å. A stretching motion will accentuate that crowding. The derivative for these bonds (0.982 × 10^{-30} C m/V) is decreased from that in the chair form. The origin of this reduction is presumed to be similar to that of H* in the *gauche* alkanes. The derivative for Hm_1 (●, 1.275 × 10^{-30} C m/V) is slightly larger than that for Heq in **e**. The derivatives for the other CH still exhibit the axial/equatorial spread but are not as exaggerated; axial, 1.043 × 10^{-30} C m/V; equatorial, 1.187 × 10^{-30} C m/V.

Methylcycloalkanes. The $\partial\bar{\alpha}/\partial r_{CH}$ data for **f**−**h** are plotted versus number of carbons in Figure 5. The evolution of axial/

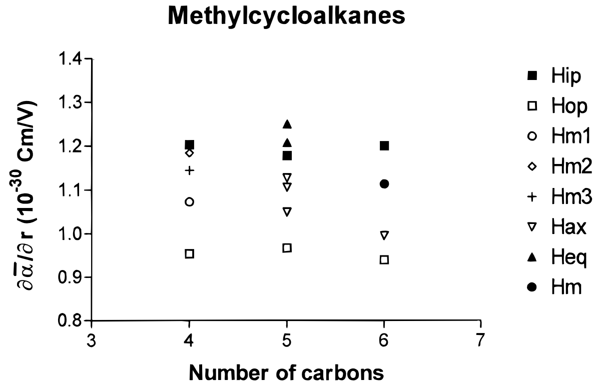


Figure 5. Calculated (HF/D95**) values of mean molecular polarizability derivative associated with the stretch of a single CH bond in methylcycloalkanes. See Figure 1 for labels.

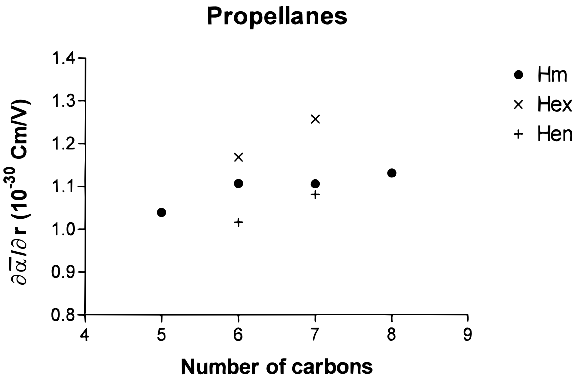
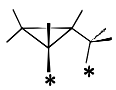


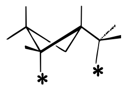
Figure 6. Calculated (HF/D95**) values of mean molecular polarizability derivative associated with the stretch of a single CH bond in propellanes. See Figure 1 for labels.

equatorial character in the ring CH with ring size is again apparent. The methyl CH are classed as Hip or Hop (Figure 1) on the basis of their alignment with the carbon skeleton, but the tilt of the methyl brings the Hop* closer to Hax*:

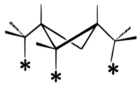
g)



h)



i)



The interatomic distances for the proximate CH* are (**g**) 2.57 Å; (**h**) 2.60 Å; (**i**) 2.59 Å. The lowered values of $\partial\bar{\alpha}/\partial r_{\mathrm{CH}}$ (Table 3) are similar to those found in the *gauche n*-alkanes and in **f**.

We note that a slightly reduced value of $\partial\bar{\alpha}/\partial r_{\mathrm{CH}}$ was found for the methyl CH bonds designated Hop in **b**. An inward tilt of the CH bonds and the inter-hydrogen distance of 2.63 Å serve to classify them as somewhat sterically crowded.

Propellanes. The propellanes (Figure 1, **j**−**m**) are highly strained molecules. First synthesized by Wiberg et al., their structure, vibrational spectra,[23,24] and equilibrium charge distributions[18,19] have been studied in some detail. The bridgehead carbon has inverted tetrahedral geometry and withdraws charge from the adjacent methylenes.[18,19] Despite the strain at the bridgehead carbon, we find no unusual behavior in the derivatives (Table 3, Figure 6). The endo versus exo distinction may be applied to some of the methylene CH bonds. The remainder are simply labeled Hm. The derivative for the Hm in **j** is almost identical to that of cyclopropane. The Hm in **k**, **l**, and **m** are slightly elevated above the benchmark value for methane and seem be the result of an averaging of their dual axial and equatorial character. The endo or exo classification separates the CH that are axial to the larger ring segment, pointing inward, from those equatorial to it, pointing out away from the molecule. The derivatives for the Hex bonds are always larger than for the Hen. The explanations presented above for the decrease (Hop, Hax, H*) or increase (Hip, Heq, H*) are assumed to apply here as well.

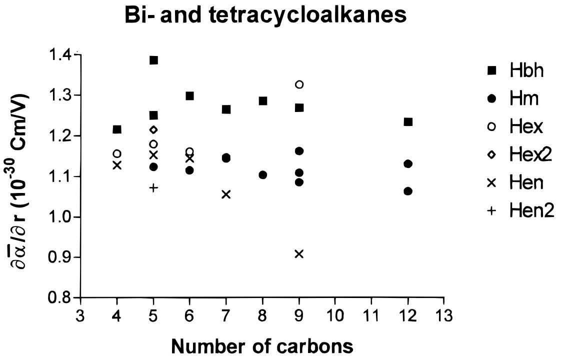


Figure 7. Calculated (HF/D95**) values of mean molecular polarizability derivative associated with the stretch of a single CH bond in bi- and tetracycloalkanes. See Figure 1 for labels.

Bicycloalkanes. The CH bonds in the bicycloalkanes (Figure 1, **n**−**u**) are described as Hm, Hax, Heq, Hen, Hex, and the final new category, the bridgehead hydrogens, Hbh. The bridgehead hydrogens have the greatest polarizability derivative of any CH bonds studied so far (Table 3, Figure 7). Most of the derivatives for the methylene CH exhibit the axial versus equatorial or endo versus exo patterns, but there are some notable exceptions, discussed below. The relative magnitudes of the polarizability derivatives can be predicted immediately from their classification as endo or exo, just as in the propellanes. The Hex are equatorial to the larger ring and produce a greater change in the molecular polarizability when they are stretched. The endo are axial to the larger ring and have smaller derivatives.

The bridgehead CH bonds are located at the nexus of three chains. Most of the enhancement might be explained in terms of the ease of charge displacement along the several carbon chains, as has been found for the Hip in the straight-chain alkanes or the Heq in the cycloalkanes. The role of the highly strained bridgehead carbon is not yet well-understood. The derivative for Hbh is always greater than 1.20×10^{-30} C m/V but does not increase with ring size. In fact, the largest derivative, 1.38×10^{-30} C m/V, appears in one of the smallest molecules bicyclo[1.1.1]pentane (Figure 1, **n**). We have considered the angle of the bond relative to the carbon skeleton and to the bridgehead hydrogen opposite, orientation relative to the principal axes of the equilibrium polarizability tensor, and group strain, but no simple explanation for this unusual intensity has been identified. We are presently carrying out a full AIM analysis of this molecule and plan to measure the absolute Raman trace scattering intensities, in order to test the validity of the predicted derivatives and to gain a greater understanding of their origin.

Bicyclo[3.3.1]nonane (**u**) presents some very interesting CH bond types. The derivatives illustrate the cumulative importance and interplay of the factors considered so far. The derivative for the bridgehead CH is quite large but less than that in **n**. The tilt of the bridgehead hydrogen relative to the carbon skeleton may offset the enhancement owing to its location at the end of three carbon chains; reduced strain may also be a factor. As with its counterparts in **k**, **l**, **o**, and **p**, the Hm_1 bond is equatorial to one ring and axial to the other, structurally identical ring. The derivative of 1.108 × 10^{-30} C m/V is therefore intermediate to typical axial and equatorial values. The bonds labeled Hm_2 and Hm_3 are pseudo-axial and pseudo-equatorial, respectively, to a single ring. The derivatives of 1.085 and 1.162 × 10^{-30} C m/V are comparable to those for Hax and Heq in the simple cycloalkanes.

The Hex bond is equatorial to a single ring, but its derivative is much greater than expected, exceeding even that of the bridgehead bond. This makes more sense when the position and orientation are taken into account:

(1) it is both exo and equatorial with respect to the cyclohexane ring;

(2) it is aligned with the three-carbon chain terminating at Hbh, just as the methyl Hip's in propane are aligned with the carbon chain; some interplay may occur;

(3) there may be unusual interaction between Hex and the sterically crowded Hen.

The Hen bond has an axial orientation to the ring, so it is not expected to have a large derivative. In addition, the two Hen bonds are pointed toward each other, only 2.015 Å apart, so that the steric crowding is highly significant. In this circumstance, we expect a decrease in the derivative, as has been observed for the crowded CH* bonds. This expectation is borne out in the predicted value of 0.908 × 10^{-30} C m/V for $\partial\bar{\alpha}/\partial r_{CH}$. We speculate that the atomic electron populations of Hen and Hex at equilibrium, and the charge flow between them during a vibration, may be affected by the steric hindrance. Greater insight should be obtained after an AIM analysis of the molecular wave functions, currently in progress.

Tetracyclane. The tetracyclo[5.3.1.$1^{2,6}$.$0^{4,9}$]dodecane (iceane, **v**) has only three types of CH bond: Hbh, Hm_1, and Hm_2. The derivative for Hbh is large, though less than in other bridged molecules. From its structure, it is likely to be less strained than those molecules, and this may be a relevant factor. The Hm_1 are not crowded and are axial to the chair form cyclohexane. The Hm_2 are sterically crowded and are equatorial relative to the chair form cyclohexane. The competing characteristics yield intermediate values for the derivatives. The derivative for the Hm_2 is greater than that for Hen in **u**, though much lower than a typical equatorial CH. The derivative for Hm_1 similarly reflects the blending of the axial and exo characters. For each, the exo or endo aspect predominates over the axial or equatorial. When taken along with the endo and exo pair from **u**, we find the following sequence for $\partial\bar{\alpha}/\partial r_{CH}$ (units of 10^{-30} C m/V):

Hen (**u**) {axial, endo}	0.908
Hm_2 (**v**) {equatorial, endo}	1.063
Hm_1 (**v**) {axial, exo}	1.130
Hex (**u**) {equatorial, exo}	1.325

Summary of Factors Affecting the Magnitude of the Polarizability Derivative. While a number of different labels have been applied to the different CH bonds in the 35 molecules, several of these may be thought of as different manifestations of the same underlying factors. Having examined the molecules in some detail, we are now in a position to extract some principles that appear to govern the magnitude of the polarizability derivatives. The principal factors are summarized here, with some typical examples:

location, increase in derivative for a bond at or near the end of the molecule; seen with Hip, Hop versus Hm (straight chain);

alignment, increase in derivative for a bond aligned with an all-*trans* carbon skeleton or with a ring plane; seen with Hip (straight chain), CH● (*gauche*), Hex, Heq (cyclic);

steric hindrance, reduction in derivative for CH bonds pointed toward the interior of the molecule, and toward each other; seen previously in *gauche* straight-chain alkanes, and here for CH* (**f**−**i**) and for Hen (polycyclic);

group strain, increase in derivative when the atom being displaced is attached to a carbon atom under strain; exemplified by Hbh (**n-v**);

averaging, the interplay of competing effects cannot be precisely predicted at this point, though there is certainly evidence of an averaging effect; seen with Hm (**k**, **l**, **o**, and **p**), Hen and Hex in **u**, and Hm_1 and Hm_2 in **v**.

One factor that is conspicuous by its absence is the CH bond length. While the Hip and Heq are often slightly shorter than their counterparts, there is no correlation between bond length and polarizability derivative, either within a molecule, for a homologous series, or across the entire set studied here. For example, the bond length for Hbh is 1.070 Å in **r** and 1.088 Å in **u**, essentially spanning the range of calculated values; yet, the derivatives are both above average (1.216, 1.268 × 10^{-30} C m/V). The latter bond length is identical to that of Hm in the same molecule, for which the derivative is only 1.08 × 10^{-30} C m/V.

Transferability and the Bond Polarizability Model. We now consider the utility of the bond polarizability model,[7−9] in light of the previous experimental work and the present predicted values for polarizability derivatives. The model was developed in order to simplify the task of quantifying Raman scattering intensities. The basic assumptions do not include transferability; rather, they outline the approximation of the total molecular polarizability ellipsoid as a sum of bond polarizability ellipsoids. Each of these ellipsoids is described by a bond polarizability tensor whose principal axes are arranged so that the largest component lies along the bond. The other two are assumed to be identical.

In the simplest version, the change in the total molecular polarizability that can occur during a vibration may be described by the changes that occur in each bond. The derivative is expected to be nonzero only for stretching motions. The bonds are noninteracting; that is, a change in the *molecular* polarizability due to the stretch of one bond is assumed to be localized entirely to that bond. Better results may be obtained if nonzero terms are included for deformation and if some interaction is allowed. The parameters (bond polarizability derivatives) are obtained from an empirical fit of observed intensities within the dictates of the model. Transferability of the derivative for a particular motion, such as the CH stretch, seemed eminently suitable to this model and is often invoked in such analyses.[25,26]

Our approach is fundamentally different from that in the bond polarizability model. We begin by obtaining a value for the total molecular polarizability from an ab initio calculation and then get the derivative by finite difference. While we have not performed any AIM analyses for this paper, we use our previous work to interpret the present results. The hallmark of our analyses has been to seek an understanding of the polarizability derivative as the change in the charge distribution throughout the entire molecule associated with the stretch of a single bond. The same parameters are used in the experimental analyses. Does this approach preclude the possibility of applying a single, average value to experimental spectra?

In **a**, we find the average value for $\partial\bar{\alpha}/\partial r_{CH}$ to be 1.02 × 10^{-30} C m/V, close to the benchmark value for methane. Most of the derivatives are clustered at a value slightly below that for methane (Figure 4), but the predicted increase for Hip brings the average up. There are many possible conformations of this molecule at room temperature, even if it contained only a single *gauche* C−C−C link. Such conformational changes will result in the variations noted earlier in butane and pentane.[3,4] The number of similar modes, the increases and decreases in intensity, and myriad small changes in bond length serve to blend the normal stretching vibrations into seemingly continuous bands. Under these circumstances, it should be possible to use a single average parameter to fit such spectra, given that assignment of individual peaks to particular bonds is entirely out of the question. However, we emphasize that the bonds should be considered individually in any study where bands are assignable or when detailed information about structure and charge flow is sought.

The analysis of straight-chain alkane spectra has received much attention over the years.[25,27−29] Recently, the bond polarizability model was used in the analysis of the liquid-phase spectra of C_{12} to C_{20}.[25] The CH stretching vibrations were not included. For all the C−C stretch vibrations, a single value for the polarizability derivative was found to be adequate and preferable in terms of time and ease of computation. The alternative considered was to use the multiple values reported for different conformers of *n*-butane.[3,15] The success of the single parameter seems to indicate the feasibility of using an average value for long-chain hydrocarbons. However, since carbons are interior atoms, the variation of intensity with bond position may be quite different from that of the CH bonds.

Conclusions

An ab initio study of polarizability derivatives associated with the stretch of CH bonds in hydrocarbons has shown that considerable variation in these derivatives may be anticipated on the basis of molecular structure. We have categorized the predominant factors as location, alignment, steric hindrance, and group strain. Averaging of several competing factors has also been inferred. When analyzing the spectrum of fairly large molecules containing a variety of these CH bond classifications, it is not inappropriate to use an average value for the total intensity in the CH region. It cannot be forgotten that $\partial\bar{\alpha}/\partial r_{CH}$ depends on the concerted change in the charge distribution of the entire molecule. When the individual bands are resolved or the study of charge flow is important, the individual variations must be considered.

At the present time, we have begun a complete experimental study of the Raman trace scattering spectrum of bicyclo[1.1.1]-pentane along with an AIM analysis of the polarizability and derivatives. This is a very interesting molecule as it has only two kinds of CH bond, for which very different values of $\partial\bar{\alpha}/\partial r_{CH}$ have been predicted in the present work. It is hoped that this analysis may provide confirmation of the predicted variations as well as deeper understanding of their origin. In the long term, we hope to obtain AIM and/or experimental data for several other molecules, including bicyclo[1.1.0]butane and [1.1.1] propellane, as well as for longer chains. Calculation of the $\partial\bar{\alpha}/\partial r_{CC}$ in the molecules studied here is in progress. Further important applications of this research include the prediction and interpretation of Raman spectra of biologically relevant molecules and the possibility that variations in $\partial\bar{\alpha}/\partial r$ may be used as a probe of charge flow in molecules that exhibit nonlinear optical properties.

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